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(71) Applicants
Inco Limited, 1 First
Canadian Place, Toronto,
Ontario, M5X 1C4,
Canada

(72) Inventors
Einar Walli,
Kohur Nagaraja
Subramanian,
Gerald Vernon Glaum

(74) Agent
C. H. Greenstreet

(54) Separation process

(57) A slurry of iron oxide solids containing dissolved nickel and/or cobalt is treated to separate those metal(s) from the slurry. The treatment includes controlled precipitation of the sulphides of the metal(s) which is effected by contacting the slurry with calcium or

barium sulphide or both to precipitate nickel and/or cobalt sulphides. The precipitated sulphides are separated from the treated slurry by flotation for which suitable collecting agents include sulphyaryls, dithiophosphates, thionocarbamates, and dithiocarbamates and suitable frothing agents include methyl isobutyl carbinol and polypropylene glycol methyl ether.

ERRATUM
SPECIFICATION NO 2049646A
Correction made under Section 117(1) of the Patent Act 1977.
Front page. Heading (72) Inventors below Gerald Vernon Glaum insert Victor Alexander Ettel

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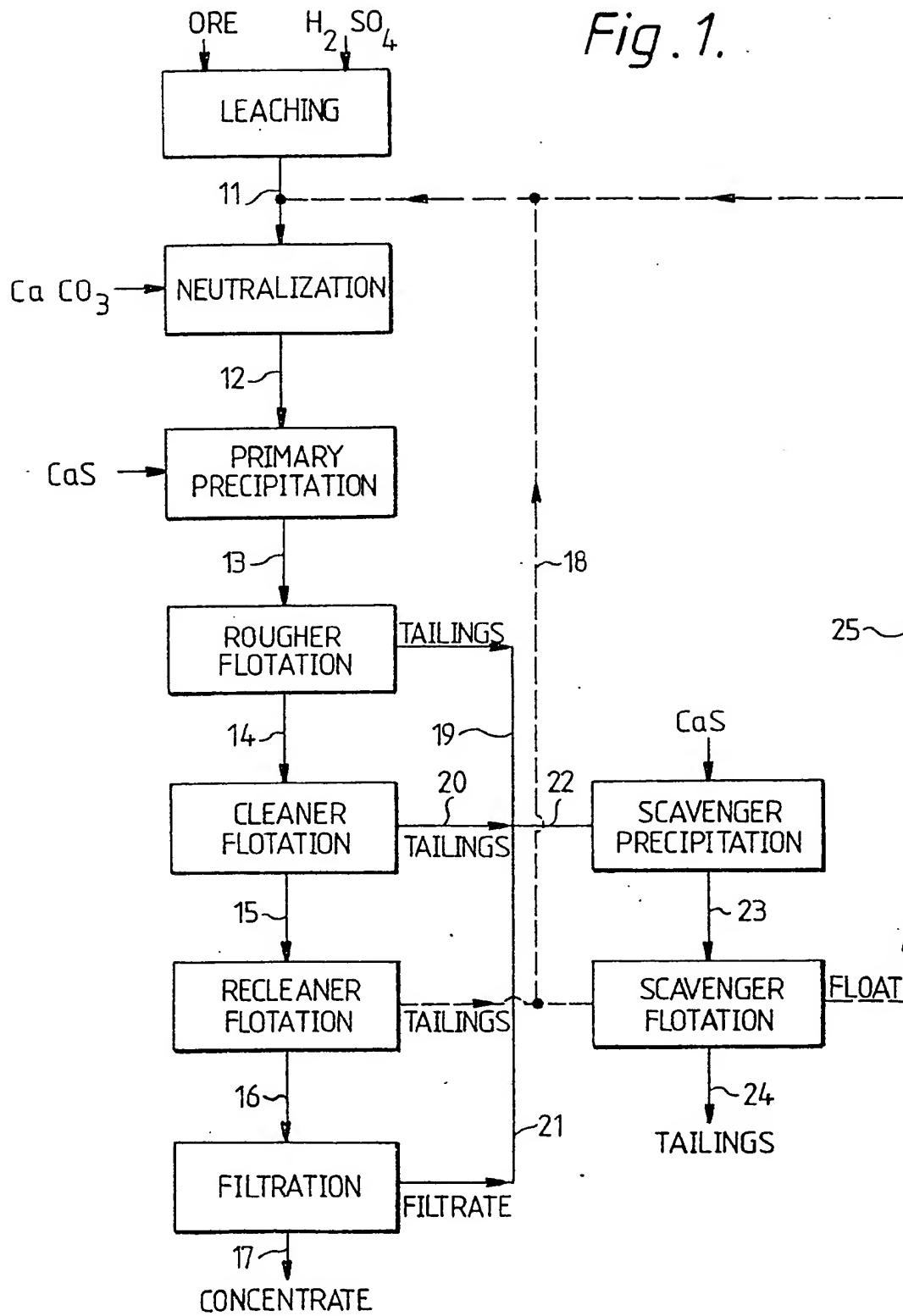
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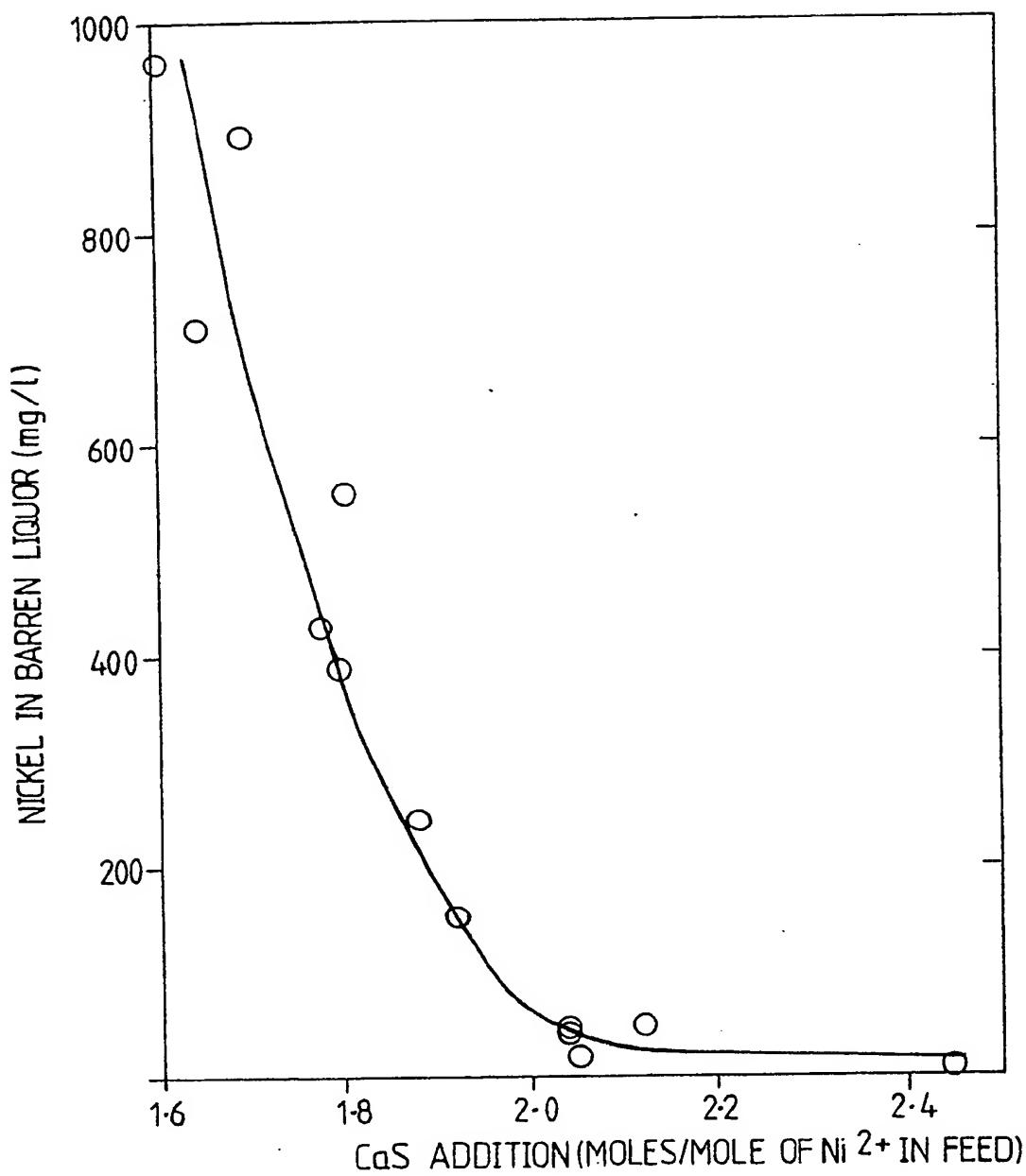
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Fig. 2.



Primary precipitation followed by three stage flotation yielded a concentrate containing over 33% nickel and representing about 7.7% of the recoverable nickel. The other constituents of the concentrate were: 3.3% Co, 8% Fe, 0.04% Mn, 0.5% Ca, 0.5% Mg, 2.0% Al and 36% S. The amount of iron in the concentrate corresponded to about 0.5% of the total iron in the slurry.

5 The filtrate separated from the recleaner concentrate was combined with the tailings of the rougher and cleaner floatations and subjected to scavenging. This operation consisted of a precipitation and a one-stage flotation. The precipitation differed from the primary precipitation only in the amount of calcium sulphide used. For the scavenging precipitation 4.64 moles of CaS were used per mole of (Ni²⁺ + Co²⁺) present in the scavenger feed. The results of the scavenging are shown in Table 5. 5

TABLE 5

Stream	Weight or Volume of Stream	Ni Analysis of Stream	Distribution* of Ni in Stream
Scavenger feed solids	2286 g	0.08 %	5.84
Scavenger feed solution	8.95 l	0.416 g/l	11.3
Scavenger concentrate	253.2 g	1.25 %	9.85
Scavenger filtrate	2231.5 g	0.08 %	5.85
Scavenger filtrate	16.3 l	0.035 g/l	1.77

*expressed as percentage of total nickel in initial slurry.

It will be seen that the scavenger concentrate contains about 10% of the total nickel available in the leach slurry. Refinements to the scavenger flotation, eg adoption of multistage flotation, could provide a higher nickel grade in the scavenger concentrate. Redissolution of precipitated nickel from the scavenger concentrate in incoming slurry may be effected by any known technique.

15 CLAIMS

1. A process for separating dissolved nickel, cobalt or both from an aqueous slurry of iron oxide solids which comprises precipitating the nickel, cobalt or both as sulphides by reaction of the slurry, in two or more reactors connected in series, with calcium sulphide, barium sulphide or both at an initial pH of not more than 4 but not so low that hydrogen sulphide is formed and at a temperature of at least 20 60°C, the residence time of the reaction mixture in the first reactor being not more than 15 minutes, and separating the precipitated sulphides from the reaction mixture by flotation. 20

2. A process claimed in claim 1, wherein the slurry is contacted with calcium sulphide and/or barium sulphide at a temperature in the range from 60 to 80°C.

3. A process as claimed in claim 1 or wherein precipitation is effected by continuously feeding the 25 aqueous slurry of iron oxide solids and an aqueous slurry of calcium sulphide or barium sulphide or both into the reactors.

4. A process as claimed in any preceding claim, wherein the residence time in the first reactor is less than 3 minutes.

5. A process as claimed in any preceding claim wherein the initial pH of the slurry of iron oxide 30 solids is in the range from 2 to 3.

6. A process as claimed in any preceding claim, wherein of pH of the reaction mixture is controlled so that it does not exceed 4 during precipitation.

7. A process as claimed in any preceding claim wherein the amount of calcium and/or barium sulphide used and the overall reaction time are so selected that at least 50 mg/l of the nickel and/or 35 cobalt remain in the solution at the end of the precipitation.

8. A process as claimed in claim 7, wherein from 100 to 300 mg/l of the nickel and/or cobalt remain in solution at the end of precipitation.

9. A process as claimed in claim 7 or 8, further comprising the steps of treating the tailings slurry from the flotation with additional amounts of calcium and/or barium sulphide at a temperature from 60 40 to 80°C to precipitate substantially all the remaining nickel and/or cobalt as sulphide(s) and separating precipitated sulphides from the reaction mixture by flotation.

10. A process as claimed in claim 9, wherein the sulphide(s) separated out by the flotation of the treated tailings slurry are recycled by dissolution in fresh slurry to be treated.

11. A process for separating dissolved nickel or cobalt or both from an aqueous slurry of iron oxide 45 solids substantially as hereinbefore described, with reference to the accompanying drawings.

TABLE 3

Test	Sulphiding Agent	Amount of Sulphiding Agent (S ²⁻ as % of ore wt.)	Concentrate Analysis (%)			% Recovery of Ni in concentrate
			Ni	Fe	S	
G	CaS	2.1	14.7	23	18.4	89
H	H ₂ S	4.5	6.2	37	22	95

EXAMPLE 4.

The effect of varying the amount of sulphiding agent used on the residual nickel content of the tailings after flotation and on the grade (with respect to Ni) of the concentrate was investigated. For 5 these tests the preferred apparatus consisting of a 'T' shaped reactor followed by a conventional vessel was employed. The residence time in the 'T' reactor was less than 3 seconds. The overall residence was found not to be critical and a five minute residence was used for each of the tests. The amount of calcium sulphide used was chosen to achieve various levels of precipitation and in each case the 10 concentrate obtained after a three stage flotation was analysed. Figure 2 shows a plot of the nickel content of the barren liquor, ie mg/l of nickel left in solution after the precipitation process, as a function of the amount of sulphiding agent used (expressed in moles of CaS per mole of Ni²⁺ dissolved in the original slurry). From the graph it can be seen that very large amounts of sulphiding agent have to be used to achieve total precipitation of the nickel. The efficiency of the sulphiding agent drops sharply as the nickel content of the barren liquor drops below about 50 mg/l.

15 Figure 3 shows the effect of attempting to lower the residual amount of dissolved nickel on the concentrate grade (% Ni in the concentrate). The concentrate grade begins to fall as residual dissolved nickel falls below about 200 mg/l or so and then falls sharply when the nickel content of the barren liquor falls below about 50 mg/l. The nickel recovered in the concentrate is also maximised at a residual nickel level of about 200 mg/l. Above this level recovery decreases slightly. However, at lower levels of 20 residual nickel, most particularly below 50 mg/l, the nickel recovery also falls very sharply. The reasons for this decrease in flotation recovery are not known but may involve decreased reactivity of the surface of the sulphide precipitate with the flotation collector.

The above results show that a residual level of dissolved nickel of from 100 to 300 mg/l gives 25 efficient utilization of the sulphiding agent, good nickel recovery and a high grade of concentrate. The information was used in designing the process shown in Figure 1.

EXAMPLE 5.

A test was carried out using this process on a slurry similar to that used for the previously 30 described tests. The pH of the slurry was adjusted to 2 and primary precipitation was carried out using a 'T' reactor for the initial stage. The precipitation temperature was 80°C, with a 5 minute total residence time. The amount of calcium sulphide added corresponded to 1.37 moles per mole of (Ni²⁺ + Co²⁺) present in the slurry. After precipitation, flotation was carried out at 55°C in three stages. Analyses of the various streams were performed and the results are shown in Table 4.

TABLE 4

Stream	Weight or Volume of Stream	Ni Analysis of Stream	Distribution * of Ni in Stream
Leach slurry solids	2284 g	0.10 %	6.9
Leach slurry solution	4.31 l	7.17 g/l	93.1
Rougher tailings solids	2071.8 g	0.08 %	5.00
Rougher tailings solution	6.27 l	0.377 g/l	7.13
Cleaner tailings solids	214.2 g	0.13 %	0.84
Cleaner tailings solution	2.10 l	0.529 g/l	3.35
Recleaner tailings solids	38.0 g	4.29 %	4.92
Recleaner tailings solution	1.30 l	0.291 g/l	1.14
Recleaner float solids	76.0 g	33.5 %	76.8
Recleaner float solution	0.575 l	0.481 g/l	0.83

*expressed as percentage of total nickel in the feed slurry.

TABLE 1

Test	Final pH	Concentrate Analysis (%)			% Recovery of Ni in concentrate
		Ni	Fe	S	
A	2	12.9	38	12.9	74
B	3	15.6	33	18.3	93
C	4	8.8	41	9.5	71

The results of the tests indicate that pH 3 gives the best results in terms of nickel recovered in the concentrate and concentrate grade. For test (B) the analyses of the various streams were as follows. The cleaner tailings assayed 0.17% Ni and 56% Fe, representing 2.3% of the nickel in the feed. The rougher tailings assayed 0.09% Ni and 46% Fe, representing 4.4% of the nickel in the feed. The barren solution from the filtration step contained 0.01 g/l Ni and 7.3 g/l Fe, representing 0.2% of the feed nickel.

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EXAMPLE 2.

To investigate the effect of precipitation temperature, a second set of experiments was carried out. The final pH was set at 3 and a total residence time of 20 minutes (10 minutes in each of two vessels) was used. Three tests D, E and F were conducted with precipitation being carried out at 75, 60 and 45°C respectively. In each case the amount of calcium sulphide added was chosen to provide a redox potential of -300 mV (measured with respect to a standard calomel electrode). Table 2 below shows the results obtained. It will be seen that when a temperature of 45°C was used, the amount of nickel recovered in the concentrate was low and the consumption of sulphiding agent was high.

10

TABLE 2

Test	Precipitation Temp. (°C)	Concentrate Analysis (%)			% Recovery of Ni in Concentrate	*Wt. of CaS used
		Ni	Fe	S		
D	75.	14.7	23	18.4	89	4.7
E	60	18.3	23	19.9	91	4.1
F	45	13.5	22	21	64	8.7

*expressed as percentage of weight of limonitic ore.

EXAMPLE 3.

A comparison was made between the effectiveness of CaS and H₂S as sulphiding agents by carrying out two tests G and H in a similar manner to that described above. The pH was controlled at about 3 and the amount of sulphiding agent and residence times were adjusted to give a final redox potential of -250 mV. The results are shown in Table 3.

20

It was found that:

- (a) whereas a total residence time of 10 minutes (5 minutes in each stage) was required for precipitation with calcium sulphide, a total residence time of 30 minutes was needed when hydrogen sulphide was used;
- 25 (b) more than twice as much hydrogen sulphide as calcium sulphide (in molar terms) was needed to attain the same redox potential;
- (c) despite the longer residence time and greater amount of sulphiding agent, used the concentrate recovered using hydrogen sulphide was of a much poorer grade, the nickel to iron ratio in this concentrate being only 1:6 by weight, compared to 1:1.6 for the concentrate produced when calcium sulphide was used.

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2 In this way a high-grade nickel concentrate is obtained on subsequent flotation. After separation of this concentrate the balance of the nickel which was present in the feed slurry is in the liquor or solids of the tailings of the flotation. Most of this nickel may be recovered by subjecting the tailings to a further sulphidation. For this sulphidation the same sulphiding agents, temperature, and pH conditions as 5 before are used, except that the amount of sulphiding agent is chosen to result in essentially complete 5 precipitation of the nickel. The slurry is then subjected to flotation and a nickel concentrate of comparatively low grade is recovered. This concentrate, containing, say, 10 to 15% of the total dissolved nickel present in the feed may be recycled by redissolving it in fresh feed slurry. In this overall process up to 98% of the dissolved nickel present in a feed slurry has been recovered.

10 The control of the end point by means of the amount of sulphiding agent used may be 10 accomplished in any convenient manner. For example, redox potential measurement may be used for monitoring the progress of the reaction, although it has been found that such measurements are not very reliable. It is preferred to monitor the nickel content of the liquor during the reaction and add the sulphiding agent accordingly.

15 To concentrate the nickel sulphide produced by the precipitation a multistage flotation is desirable, 15 and it is preferred to carry out the flotation on the hot reacted slurry. Suitable collecting agents include sulphhydryls, dithiophosphates, thionocarbamates and dithiocarbamates. Suitable frothing agents include methyl isobutyl carbinol and polypropylene glycol methyl ether.

A separation process according to the invention will now be described with reference to Figure 1 20 of the accompanying drawings, which is a flow chart illustrating a preferred process according to the 20 invention.

Referring to Figure 1, a limonitic ore containing nickel and cobalt and large amounts of iron is 25 leached with sulphuric acid to produce a slurry 11 comprising a cobalt-and-nickel-containing liquor and iron oxide solids. The pH of this slurry is adjusted to a value of 2—3 by addition of calcium carbonate.

25 The treated slurry 12 is then subjected to primary precipitation, which is carried out at a temperature in the range from 60—80°C, in two stages, using an aqueous slurry of calcium sulphide as the sulphiding 25 agent. Insufficient calcium sulphide is used for complete precipitation of the nickel present in solution.

The resulting slurry 13 which contains nickel sulphide and iron oxide solids is subjected to a three-stage flotation. The first stage, or rougher flotation, produces a float product 14 which is fed to the 30 second stage, or cleaner flotation. The float product 15 from the cleaner flotation is fed to the final stage or recleaner flotation to produce a float product 16 which is filtered to separate the nickel concentrate 17.

30 The tailings 18 from the recleaner flotation may be recycled to redissolve precipitated nickel in fresh leach slurry 11, or may be passed to the scavenger flotation.

35 Tailings 19 and 20 from the rougher and cleaner flotation respectively are combined with filtrate 35 21 obtained from the filtration step to form a slurry 22 which is subjected to further precipitation and flotation. This scavenger precipitation is carried out in the same manner as the primary precipitation except that the amount of calcium sulphide added is sufficient for complete precipitation of the dissolved nickel. The resulting slurry 23 is subjected to scavenger flotation. The tailings 24 from this 40 operation contain most of the iron oxide in the original feed and very little of the nickel. The concentrate 25 obtained from the scavenger flotation is of inferior nickel grade to the concentrate 17. The concentrate 25 is recycled to the stream 11 of incoming slurry to redissolve precipitated nickel.

A number of experiments were performed to determine the effect of such parameters as pH, 45 temperature and sulphiding agent on the precipitation. A simplified version of the process whose flow 45 chart is shown in Figure 1 was used. No scavenging was carried out and no recleaner flotation was carried out. The float product from the cleaner flotation was simply filtered and assayed. All the percentages given are by weight unless otherwise specified.

All the tests were carried out on a slurry derived from the leaching of a limonitic ore containing 50 1.5% Ni, 0.15% Co and 47% Fe with sulphuric acid. The leaching was affected at 240—255°C with an 50 amount of sulphuric acid corresponding to 20—25% of the ore weight with an initial pulp density of from 26 to 31% solids. An assay of the slurry at a pH in the range from 2 to 2.5, showed that the solids content was 27% of which 0.1% was Ni and 50% was Fe. The liquor contained, in grams per litre (g/l): 5.3 Ni, 0.49 Co, 3.2 Mn, 1.0 Fe, 0.64 Mg 2.2 Al, 0.1 Cr and 1 to 10 H₂SO₄. The distribution of nickel in the slurry was about 93% in the liquor and 7% in the solids.

55 EXAMPLE 1.

Experiments were carried out to determine the effect of pH on the separation process. The slurry was treated with an aqueous slurry of a sulphiding agent prepared by pyro-metallurgical reduction of calcium sulphate, the slurry having 10% solids of which 74.7% was CaS. Precipitation was carried out using an overall residence of 15 minutes at 75°C with the pH being adjusted to give a final pH of 2, 3 60 and 4 in the respective tests. After precipitation, the two stage flotation was carried out at 20°C using potassium amyl xanthate as the collector and polypropylene glycol methyl ether as the frother. Table 1 shows the analysis of the concentrates obtained in the tests.

SPECIFICATION
Separation process

This invention relates to a process for separating dissolved nickel or cobalt or both from an aqueous slurry of iron oxide solids.

5 There are substantial reserves of sulphide and oxide ores that contain small amounts of nickel and/or cobalt and large amounts of iron. In some processes for recovering the nickel or cobalt from such ores the first step is to leach the ore with an acidic liquid. This gives a slurry of hydrated iron oxide solids in a liquor containing small amounts of dissolved nickel and/or cobalt. The slurry is allowed to settle and then the liquor is decanted or filtered off and treated to recover the nickel or cobalt. The solid/liquid separation is not easy because the iron oxide tends to be in finely divided form. For this reason, the 10 separation process contributes significantly to the cost of recovering the metals.

It has now surprisingly been found that by using suitable sulphiding agents and conditions, the slurry may be treated without first separating off the iron oxide so as to precipitate nickel and/or cobalt sulphides which may be separated from the iron oxide by means of flotation.

15 The present invention provides a process for separating dissolved nickel, cobalt or both from an aqueous slurry of iron oxide solids which comprises precipitating the nickel, cobalt or both as sulphides by reaction of the slurry, in two or more reactors connected in series, with calcium sulphide, barium sulphide or both at an initial pH or not more than 4 but not so low that hydrogen sulphide is evolved and at temperature of at least 60°C, the residence time of the reaction mixture in the first reactor being not 20 more than 15 minutes, and separating the precipitated sulphides from the reaction mixture by flotation.

Metals such as nickel have in the past been separated from solutions thereof by precipitation of the appropriate sulphide. This is usually effected by treating the metal-containing solution with hydrogen sulphide. However, this procedure is not suitable for the separation of nickel or cobalt from a slurry containing substantial amounts of iron oxide because the hydrogen sulphide also reacts with the 25 iron oxide. As a result large quantities of hydrogen sulphide are used and sulphides of iron are mixed with the nickel and/or cobalt sulphides. Thus, if a slurry of iron oxide containing dissolved nickel and/or cobalt salts is treated with hydrogen sulphide and then subjected to flotation, the sulphide concentrate obtained is of poor grade with respect to nickel and/or cobalt.

30 A commercially viable separation process relying on precipitation of sulphides should involve efficient use of the sulphiding agent (ie the calcium or barium sulphide) and good recovery of nickel and/or cobalt uncontaminated by appreciable quantities of iron from the solution.

In the description which follows reference will be made to separation of nickel from an iron-containing slurry, as the behaviour of cobalt is similar to that of nickel.

The temperature of the slurry must be maintained at at least 60°C during the precipitation. At 35 lower temperatures the amount of nickel recovered in the flotation concentrate decreases markedly. However, above 80°C, any further increases in temperature do not result in any further benefit and for this reason the temperature of the slurry is preferably maintained in the range from 60 to 80°C.

The pH of the slurry during precipitation is important to the success of the process. In order to achieve selective sulphidation and good floatability of the precipitated nickel sulphide precipitation 40 should occur at a pH no higher than about 4.5. Because the pH tends to rise during precipitation, the initial pH of the slurry must not exceed 4. Indeed, it is preferred that the pH of the slurry does not exceed 4 during precipitation. However, very acidic conditions should also be avoided because in such conditions, the sulphiding agent may be partially converted to hydrogen sulphide. Hydrogen sulphide is environmentally objectionable and adversely affects the efficiency of utilization of the sulphiding agent.

45 Accordingly if the pH of the slurry is very low (eg pH 1 or less) as in the case of slurries obtained by acid leaching, it is preferably raised to 2 to 3. This may be effected by adding lime or limestone to the slurry.

The precipitation of the nickel sulphide is carried out in more than one stage by using at least two precipitation vessels. The term "vessel" is used herein in a very broad sense to denote any apparatus within which the nickel-containing slurry is contacted with the sulphiding agent at a temperature of at 50 least 60°C. Thus the hot nickel-containing slurry and an aqueous slurry of the sulphiding agent may be fed separately to a small tank and then passed to a larger tank. The flow rate should be such that the residence time in the first tank is less than 15 minutes, preferably 3 minutes or less. In a preferred embodiment of the invention, the first stage of the precipitation occurs in a conduit rather than a tank. The hot nickel-containing slurry and the sulphiding agent are fed to two different arms of a "T" shaped 55 junction, the third arm of which discharges the partially reacted mixture into a tank. The "T" junction constitutes a first vessel in which some precipitation occurs during a very short residence time of a few seconds.

Although the precipitation can be carried out as a batch process, continuous precipitation is preferred as it is easier to control a continuous process so as to achieve a specified end point for the 60 reaction.

The amount of sulphiding agent used is selected in accordance with the extent of precipitation desired. It has been found that complete sulphidation of the nickel adversely affects both the utilization of sulphiding agent and the nickel content of the product. A preferred end point is one which leaves at least 50 mg/l, and preferably 100 to 300 mg/l, of nickel in solution.

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Fig. 3.

